Ab initio calculations of the collision-induced dipole in He–H_2. I. A valence bond approach[a)]

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(Received 4 May 1978)

The collision-induced dipole in the system He–H_2 is calculated in the multistructure Valence Bond method, using the nonorthogonal monomer orbitals. In the region around the collision diameter, which contributes most to the collision-induced ir absorption, the long range results (the leading terms are the quadrupole-induced dipole on He with R^{-4} dependence and the dispersion dipole with R^{-7} dependence) are modified by overlap effects. The short range behavior is determined, moreover, by the appearance of other important terms, the exchange dipole and the overlap-induction dipole on H_2, which vanish in the long range. Since all the short range contributions have approximately the same (exponential) dependence on the intermolecular distance, they can be collected and added as a single exponential dipole function to the R^{-4} and R^{-7} long range terms. Of the latter terms the R^{-7} dispersion dipole is of little importance.

I. INTRODUCTION

During a collision between two unlike atoms or molecules the intermolecular interaction generates a dipole moment in the collision complex, which for obvious reasons is called a "collision induced dipole." Because collision induced dipoles are a function of the intermolecular separation, the relative orientation of the molecules and the intramolecular vibrational coordinates, they give rise to absorption and emission of radiation involving all three types of degrees of freedom.[1] The absorption and emission due to translational and rotational motion are observed as broad bands in the far infrared (100–600 cm^{-1}); the collision induced vibrational transitions are associated with much shorter wavelengths, for instance the vibrational transitions of H_2 lie around 4500 cm^{-1}.

Much work has been done on the measurements of these spectra, see, for instance, Ref. 2 or the compilation of Rich and McKellar[3] for extensive literature surveys. Since the pioneering work of Van Kranendonk[4] and Poll and Van Kranendonk[5] much effort has also been put into the development of a theory explaining the line shapes. For a review of these theories we refer to Ref. 1.

Considerably less attention has been paid to the mechanism that yields the collision induced dipole itself, and especially the influence of the short range effects, such as exchange and penetration, has rarely been studied; consequently their role in the induction mechanism is at present not well understood. More has been written about the long range forces, and in particular the importance of a permanent multipole on one molecule inducing a dipole on the other has often been stressed, as it gives the leading contribution in a $1/R$ expansion of the dipole moment.[6,7] This effect is of course absent in the collision of two noble gas atoms. Here, the long range induced dipole is caused by the London dispersion forces as has been discussed in Refs. 10 and 11.

The few papers that deal with short range forces all consider pairs of atoms. Matcha and Nesbet[12] performed some SCF calculations on noble gas pairs, and Lacey and Byers Brown[13] did first order perturbation calculations on the same systems and a few other atomic pairs. Nobody to date, however, has included the relevant long and short range effects in one single calculation; hence the question of the relative importance of these effects is still undecided.

In this paper we will consider long and short range contributions to the collision induced dipole for the first time within one formalism: the multistructure valence bond (VB) method. We have chosen to undertake this study on the He–H_2 system for several reasons: In the first place the induced vibrational spectrum has been interpreted recently,[14] enabling a comparison of the calculations with the experiment (although a comparison with the results of this paper is only partially possible, since the translational band has not yet been interpreted and we do not consider changes in the vibrational coordinate. In a second paper we will give a more detailed analysis including vibration). A second reason for the choice of He–H_2 is that we have previously calculated part of its potential energy surface,[15] also using the VB formalism so that we had a wavefunction at our disposal. (It has appeared that the dipole moment could not be directly calculated from this wavefunction, however, since it is much more sensitive to orthogonalization of the orbital basis than the interaction energy). Finally, mixtures of noble gases with H_2 belong to the most widely investigated systems, and He–H_2 is the simplest example of such a mixture, al least from the quantum chemist's point of view.

As has been pointed out before,[16] the VB method changes for increasing intermolecular distance into an ordinary perturbation method. One can use this feature of VB as a selection criterion for VB structures; that is, one includes in the calculation only the VB structures that are known to give important contributions in the long range. Doing this, one assumes implicitly that short range forces are not yet so dominant in the region of interest that they make a modelling after long range theory impossible. Our experience with calculations around the Van der Waals minimum is that this

[a)]Supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

assumption holds reasonably well for the energy, and it is interesting to see whether this also works for the dipole moment, especially since the distances of interest are somewhat shorter in this case. The region most sensitively probed by the experiment ranges from 4.5–8 bohr and the sensitivity peaks just inside the scattering diameter.

II. THEORY

The valence bond method is a variational method; therefore it requires the solution of a secular problem with the Hamilton matrix elements having the following form:

$$\langle Y\Phi_a^A\Phi_b^B | H^A + H^B + V | Y\Phi_{a'}^A \Phi_{b'}^B \rangle .$$

Here H^A is the Hamiltonian of monomer A, H^B of monomer B, and V describes the interaction between the two. The operator Y is the spinfree equivalent of a singlet spin projector times the antisymmetrizer; it is a linear combination of all electron permutations. In this work Y is an NP-type Young projector and hence our VB structures are the spinfree equivalents of spin-bonded functions.[17] The ath excited state Φ_a^A of molecule A is a product of SCF orbitals obtained from a Hartree–Fock calculation on the free monomer; Φ_b^B is constructed analogously. In accordance with the usual second order perturbation theory for long range forces[18] only singly excited states on each of the monomers are taken into account. This means that we do not take intramolecular correlation into consideration.

Two different spin coupling schemes are possible: A and B can both be excited to a triplet or to a singlet state. Since we have found earlier[15] that the VB structures arising from triplet–triplet coupling hardly mix into the VB ground state of the complex, we do not include these kinds of states.

For larger intermolecular distances the differential overlap between orbitals on A and B becomes negligible, and hence Y factorizes effectively into a product of two singlet Young projectors Y^A and Y^B, with Y^A acting on the electrons of A only and Y^B acting on the electrons of B.

As we have discussed earlier,[16] the solution Ψ_{VB} of the secular problem corresponding to the lowest energy, may be thought of as having been obtained in the long range from a perturbation treatment (PT) in a finite basis. Defining the resolvent R_0 of the unperturbed Hamiltonian $H^A + H^B$ in this basis[19]:

$$R_0 \equiv \sum_{a,b}{}' \frac{|ab\rangle\langle ab|}{\Delta E_{ab}},$$

where $|ab\rangle = |Y^A\Phi_a^A\rangle |Y^B\Phi_b^B\rangle$, and

$$\Delta E_{ab} = (E_0^A - E_a^A) + (E_0^B - E_b^B)$$

we can write[19]:

$$|\Psi_{PT}\rangle = (1 + R_0V + R_0VR_0V + \cdots)|00\rangle .$$

Here we have used that the first order interaction is zero in the long range.

The dipole moment of the complex can now be approximated by:

$$\langle \mu_{PT}\rangle = \langle \Psi_{PT} | \mu | \Psi_{PT}\rangle ,$$

where $\mu = \mu^A + \mu^B$ and $\mu^A = \sum_{\alpha\in A} \mathbf{r}_\alpha q_\alpha$ (a sum over the particles α of A, which have charges q_α and position vectors $\mathbf{r}_\alpha$). An analogous definition holds for μ^B. Using the above perturbation expansion of Ψ_{PT} one writes through second order in V for $\langle\mu_{PT}\rangle$:

$$\langle \mu_{PT}\rangle = \langle 00 | \mu^{(0,0)} + \mu^{(1,0)} + \mu^{(1,1)} + \mu^{(2,0)} | 00\rangle , \tag{1}$$

where the effective dipole moment operators are given by:

$$\begin{aligned} \mu^{(0,0)} &= \mu \\ \mu^{(1,0)} &= \mu R_0 V + V R_0 \mu \\ \mu^{(1,1)} &= V R_0 \mu R_0 V \\ \mu^{(2,0)} &= \mu R_0 V R_0 V + V R_0 V R_0 \mu . \end{aligned} \tag{2}$$

The first contribution to $\langle\mu_{PT}\rangle$, which is of zeroth order in V, is the vector sum of the permanent moments on the monomers; this contribution is zero for He–H_2. The term of first order in V corresponds to a permanent moment on A inducing a dipole on B plus a permanent moment on B inducing a dipole on A. We will elaborate the matrix element $\langle 00|\mu^{(1,0)}|00\rangle$ in the appendix, where a formula is derived for the induced dipole in a pair of molecules of arbitrary symmetry. For the complex under consideration only part of the (1, 0) contribution occurs, because He does not have any multipole moment. The third and fourth terms have no classical counterparts, we will refer to them as (1, 1) dispersion and (2, 0) dispersion, respectively. Byers Brown and Whisnant[10] have named these terms dispersion of type II and type I, respectively.

Although the solution of the secular problem contains in principle a superposition of all orders of perturbation, we can nevertheless separate to a certain extent the different orders of perturbation within the VB framework by relying on the high symmetry of the monomers and assuming that third and higher order effects are negligible. In order to explain the procedure we need a few definitions. The He states of different symmetry species (i.e., of different L-quantum number) and of different symmetry subspecies (i.e., of different M-quantum number) are labelled by λ. The indices λ are in 1–1 correspondence with the set of spherical harmonics or their real form, the tesseral harmonics. The latter correspondence is used to denote the λ's explicitly. Similarly μ labels the H_2 states of different symmetry; the notation common for homonuclear diatomics is used to denote μ explicitly. We can now write R_0 as follows:

$$R_0 = \sum_\lambda \sum_\mu R_0(\lambda; \mu) , \tag{3}$$

where $R_0(\lambda;\mu)$ includes a sum over all states of symmetry λ on He and a sum over all H_2 states characterized by μ.

For a linear complex lying along the z axes the multipole expansion for V through R^{-4} dependence takes the form (for neutral monomers):

$$V = R^{-3}[-2V_3(z;z) + V_3(x;x) + V_3(y;y)]$$

TABLE I. Decomposition of the effective dipole moment operators defined in (2) into symmetry adapted components for the linear case.

$$\mu^{(1,0)} = \tfrac{3}{2} R^{-4} \mu_z^{\mathrm{He}} R_0(z;\sigma_g) V_4(z; 3z^2 - r^2) + \text{Hermitian conjugate}$$

$$\begin{aligned}
\mu^{(1,1)} = {}& 3R^{-7}\{V_3(z;z)R_0(z;\sigma_u)\mu_z^{\mathrm{He}} R_0(3z^2-r^2;\sigma_u)V_4(3z^2-r^2;z)\\
&+V_3(x;x)R_0(x;\pi_{x,u})\mu_z^{\mathrm{He}} R_0(xz;\pi_{x,u})V_4(xz;x)\\
&+V_3(y;y)R_0(y;\pi_{y,u})\mu_z^{\mathrm{He}} R_0(yz;\pi_{y,u})V_4(yz;y)\}\\
&-3R^{-7}\{V_3(z;z)R_0(z;\sigma_u)\mu_z^{\mathrm{H}_2} R_0(z;\sigma_g)V_4(z;3z^2-r^2)\\
&+V_3(x;x)R_0(x;\pi_{x,u})\mu_z^{\mathrm{H}_2} R_0(x;\pi_{x,g})V_4(x;xz)\\
&+V_3(y;y)R_0(y;\pi_{y,u})\mu_z^{\mathrm{H}_2} R_0(y;\pi_{y,g})V_4(y;yz)\}\\
&+\text{Hermitian conjugate}
\end{aligned}$$

$$\begin{aligned}
\mu^{(2,0)} = {}& 3R^{-7}\mu_z^{\mathrm{He}} R_0(z;\sigma_g)\{V_3(z;z)R_0(3z^2-r^2;\sigma_u)V_4(3z^2-r^2;z)\\
&+V_3(x;x)R_0(xz;\pi_{x,u})V_4(xz;x)\\
&+V_3(y;y)R_0(yz;\pi_{y,u})V_4(yz;y)\\
&+V_4(3z^2-r^2;z)R_0(z;\sigma_u)V_3(z;z)\\
&+V_4(xz;x)R_0(x;\pi_{x,u})V_3(x;x)\\
&+V_4(yz;y)R_0(y;\pi_{y,u})V_3(y;y)\}\\
&-3R^{-7}\mu_z^{\mathrm{H}_2} R_0(s;\sigma_u)\{V_3(z;z)R_0(z;\sigma_g)V_4(z;3z^2-r^2)\\
&+V_3(x;x)R_0(x;\pi_{x,g})V_4(x;xz)\\
&+V_3(y;y)R_0(y;\pi_{y,g})V_4(y;yz)\\
&+V_4(z;3z^2-r^2)R_0(z;\sigma_u)V_3(z;z)\\
&+V_4(x;xz)R_0(x;\pi_{x,u})V_3(x;x)\\
&+V_4(y;yz)R_0(y;\pi_{y,u})V_3(y;y)\}\\
&+\text{Hermitian conjugate}
\end{aligned}$$

$$\begin{aligned}
&+3R^{-4}[-\tfrac{1}{2}V_4(3z^2-r^2;z)+V_4(xz;x)+V_4(yz;y)] \qquad (4)\\
&-3R^{-4}[-\tfrac{1}{2}V_4(z;3z^2-r^2)+V_4(x;xz)+V_4(y;yz)].
\end{aligned}$$

Here $V_3(z;z)$ stands for $(\sum_{\alpha\in A} q_\alpha z_\alpha)(\sum_{\beta\in B} q_\beta z_\beta)$ and similar definitions hold for the other interactions. In the case of a perpendicular, T shaped, complex, which can be obtained from the linear one by rotating H_2 around the y axis over 90°, we substitute:

$$V_4(z;3z^2-r^2) = -\tfrac{1}{2}V_4(z;3x^2-r^2)+\tfrac{3}{2}V_4(z;z^2-y^2)$$

into the expansion of V, in order to have again only terms which are adapted to the local symmetries (the symmetries of the subsystems).

Using (3) and (4) one can expand the effective dipole operators defined in (2), see Tables I and II. In deriving these tables we have translated the operators μ^A and μ^B to the centers of mass of the respective monomers, which is allowed for neutral subsystems.

Now we can define the different dipole moment contributions in the VB formalism. Let us agree to call a VB structure of local symmetry $(z;\sigma_g)$ which represents He in an excited state and H_2 in its ground state a "He-induction structure," then we see from Tables I and II that a calculation on a basis that consists of only the He induction structures and the ground state gives the (1, 0) part of the dipole moment. We also see from Tables I and II that He induction structures contribute to the (1, 1) and (2, 0) part, but that they only do so in cooperation with "dispersion" VB structures (singly excited on both monomers) of other local symmetry. If, for instance, the dispersion structures of $(z;\sigma_u)$ symmetry are added to the basis the He induction structures will give a contribution to the (1, 1) and (2, 0) dispersion dipoles on H_2, and to the (2, 0) dispersion dipole on He, both in the case of the linear complex.

In analogy we call a VB structure representing He in its ground state and H_2 in an excited σ_u state (linear complex) or $\pi_{z,u}$ state (perpendicular complex) an "H_2 induction structure". As can be seen from Tables I and II these structures alone do not give a long range contribution to the dipole; in the short range they give a dipole moment on H_2, which is induced by penetration of the He atom into the charge cloud of the H_2 molecule, causing incomplete screening of the He nucleus, and by the repulsive exchange force originating from the overlap. We refer to this effect as H_2 overlap-induction.

The total dipole moment $\langle\mu_{\mathrm{VB}}\rangle \equiv \langle\Psi_{\mathrm{VB}}|\mu|\Psi_{\mathrm{VB}}\rangle$ is obtained from a VB calculation including the ground state, the He induction structures, the H_2 induction structures

TABLE II. Decomposition of the effective dipole moment operators defined in (2) into symmetry adapted components for the perpendicular case.

$$\mu^{(1,0)} = -\tfrac{3}{4} R^{-4} \mu_z^{\mathrm{He}} R_0(z;\sigma_g) V_4(z; 3x^2 - r^2) + \text{Hermitian conjugate}$$

$$\begin{aligned}
\mu^{(1,1)} = {}& 3R^{-7}\{V_3(z;z)R_0(z;\pi_{z,u})\mu_z^{\mathrm{He}} R_0(3z^2-r^2;\pi_{z,u})V_4(3z^2-r^2;z)\\
&+V_3(x;x)R_0(x;\sigma_u)\mu_z^{\mathrm{He}} R_0(xz;\sigma_u)V_4(xz;x)\\
&+V_3(y;y)R_0(y;\pi_{y,u})\mu_z^{\mathrm{He}} R_0(yz;\pi_{y,u})V_4(yz;y)\}\\
&-3R^{-7}\{-\tfrac{1}{2}V_3(z;z)R_0(z;\pi_{z,u})\mu_z^{\mathrm{H}_2} R_0(z;\sigma_g)V_4(z;3x^2-r^2)\\
&+\tfrac{3}{2}V_3(z;z)R_0(z;\pi_{z,u})\mu_z^{\mathrm{H}_2} R_0(z;\delta_{z^2-y^2,g})V_4(z;z^2-y^2)\\
&+V_3(x;x)R_0(x;\sigma_u)\mu_z^{\mathrm{H}_2} R_0(x;\pi_{z,g})V_4(x;xz)\\
&+V_3(y;y)R_0(y;\pi_{y,u})\mu_z^{\mathrm{H}_2} R_0(y;\delta_{zy,g})V_4(y;yz)\}\\
&+\text{Hermitian conjugate}
\end{aligned}$$

$$\begin{aligned}
\mu^{(2,0)} = {}& 3R^{-7}\mu_z^{\mathrm{He}} R_0(z;\sigma_g)\{V_3(z;z)R_0(3z^2-r^2;\pi_{z,u})V_4(3z^2-r^2;z)\\
&+V_3(x;x)R_0(xz;\sigma_u)V_4(xz;x)\\
&+V_3(y;y)R_0(yz;\pi_{y,u})V_4(yz;y)\\
&+V_4(3z^2-r^2;z)R_0(z;\pi_{z,u})V_3(z;z)\\
&+V_4(xz;x)R_0(x;\sigma_u)V_3(x;x)\\
&+V_4(yz;y)R_0(y;\pi_{y,u})V_3(y;y)\}\\
&-3R^{-7}\mu_z^{\mathrm{H}_2} R_0(s;\pi_{z,u})\{-\tfrac{1}{2}V_3(z;z)R_0(z;\sigma_g)V_4(z;3x^2-r^2)\\
&+\tfrac{3}{2}V_3(z;z)R_0(z;\delta_{z^2-y^2,g})V_4(z;z^2-y^2)\\
&+V_3(x;x)R_0(x;\pi_{z,g})V_4(x;xz)\\
&+V_3(y;y)R_0(y;\delta_{zy,g})V_4(y;yz)\\
&-\tfrac{1}{2}V_4(z;3x^2-r^2)R_0(z;\pi_{z,u})V_3(z;z)\\
&+\tfrac{3}{2}V_4(z;z^2-y^2)R_0(z;\pi_{z,u})V_3(z;z)\\
&+V_4(x;xz)R_0(x;\sigma_u)V_3(x;x)\\
&+V_4(y;yz)R_0(y,\pi_{y,u})V_3(y;y)\}\\
&+\text{Hermitian conjugate}
\end{aligned}$$

and the dispersion structures which determine the R^{-7} contribution in the long range (see Tables I and II); the latter structures also account for part of the higher (R^{-9}, etc.) dispersion contributions. Such a VB calculation yields the coefficients in the following expansion:

$$|\Psi_{VB}\rangle = \sum_{a,b} |Y\Phi_a^A\Phi_b^B\rangle C_{ab}. \quad (5)$$

The VB dipole moment is split into three parts:

$$\langle\mu_{VB}\rangle = C_{00}^2\langle Y\Phi_0^A\Phi_0^B|\mu|Y\Phi_0^A\Phi_0^B\rangle + 2\sum_{a,b}{}' \langle Y\Phi_0^A\Phi_0^B|\mu|Y\Phi_a^A\Phi_b^B\rangle C_{ab}C_{00} + \sum_{a,b}{}'\sum_{a',b'}{}' \langle Y\Phi_a^A\Phi_b^B|\mu|Y\Phi_{a'}^A\Phi_{b'}^B\rangle C_{ab}C_{a'b'}. \quad (6)$$

Then, summarizing, we define the following contributions:

(i) The *exchange dipole* is the expectation value of μ over the ground state VB structure. This contribution, which is due to the antisymmetrization only and vanishes in the long range, is practically equal to the first term of (6) since the coefficient C_{00} is very close to unity.

(ii) The *induction dipole on He* is the dipole obtained from a VB calculation including all induction VB structures on He, together with the ground state. Analogously for the (*overlap*-) *induction dipole on* H_2. These contributions form part of the second term in (6).

(iii) The (2, 0) *dispersion dipole* is obtained from the same term as the induction dipoles, i.e., $2\sum_a'\langle Y\Phi_0^A\Phi_0^B|\mu|Y\Phi_a^A\Phi_0^B\rangle C_{a0}C_{00}$ for molecule A, but now the coefficients C_{a0} are modified by the admixture of the appropriate (2, 0) dispersion structures (see Tables I and II) in the VB calculation. Subtracting the induction dipoles defined in (ii) yields the (2, 0) dispersion dipole. This procedure is justified since the long range expansion of the second term in (6) is the following:

$$2\langle 00|\mu(R_0V+R_0VR_0V)|00\rangle = \langle 00|\mu^{(1,0)}+\mu^{(2,0)}|00\rangle,$$

which can be proved by substituting the long range results for the VB coefficients:

$$C_{ab} \simeq \langle ab|1+R_0V+R_0VR_0|00\rangle.$$

(iv) Analogously, if we substitute these coefficients into the third term of (6) and retain only the term in V^2 we find:

$$\langle 00|VR_0\mu R_0V|00\rangle = \langle 00|\mu^{(1,1)}|00\rangle$$

and, so, the (1, 1) *dispersion dipole* in VB is defined as the third term in (6) restricted to those matrix elements that yield the corresponding long range dispersion contribution (Tables I and II).

Because in VB the wavefunctions are antisymmetrized and the exact interaction operator is used instead of only the lowest terms in the multipole expansion, the dispersion terms are modified by exchange and penetration and will no longer have an R^{-7} dependence for smaller distances. The (1, 0) He induction term too will deviate from a strict R^{-4} dependence. H_2 overlap-induction will become an important contribution, as will the exchange dipole. Decreasing R we will also find that more and more matrix elements which are vanishing in the long range will be giving contributions, because of the breakdown of local selection rules, and hence that the separately distinguished contributions (i) to (iv) will no longer completely add up to $\langle\mu_{VB}\rangle$.

III. COMPUTATIONS

Two geometries of the He–H_2 complex are considered: a perpendicular, T shaped, one and a linear conformation. In both cases the intermolecular distance is varied from 4.0–10.0 bohr, whereas the H–H distance is kept fixed at 1.40 bohr.

The SCF monomer orbitals, from which the VB structures are constructed, are taken from Geurts *et al.*[15] The A.O. basis used in that reference is a H(6, 4, 1/1, 2, 1), He(6, 2, 1/1, 1, 1) G.T.O. basis, with the exponents of the polarization functions optimized for a calculation of the dispersion energy.

At the start of this work it was our intention to use the VB wavefunctions as well from Ref. 15. The VB structures in that work are derived from orthogonalized orbitals, and if one uses these the dipole induced on He by H_2 at a distance of 8.0 bohr in the perpendicular geometry comes out to be $-29.14\ 10^{-5}$ a.u. The same contribution to the dipole moment of the complex can be calculated classically. Employing the values $\alpha_0^{He} = 1.335$, $\langle Q_2^{H_2}\rangle = 0.4931$, $\langle Q_4^{H_2}\rangle = 0.3639$, and $\langle Q_6^{H_2}\rangle = 0.2365$, all calculated from the basis of Geurts *et al.*, one finds a classical value of $-23.77\ 10^{-5}$ a.u. Judging from our experience in calculating van der Waals energies this difference of about 20% between the VB and the long range result was considered too high, so we calculated the same dipole in a basis originating from the pure, and hence nonorthogonal, monomer orbitals. This gave $-23.89\ 10^{-5}$ a.u., a number in perfect agreement with the classical result. It is easy to understand why orthogonalization has such a relatively large effect: by mixing the orbitals on A with those on B, and vice versa, one contaminates the VB structures with charge transfer structures, and an amount of charge of $0.66\ 10^{-5}$ a.u. transferred from one molecule to the other is already sufficient to explain the above differences. So, because of this sensitivity of the calculated collision induced dipoles to the artificial charge transfer introduced by orthogonalization, all subsequent calculations had to be performed in a basis of VB structures derived from the original nonorthogonal monomer MO's. The method employed by us is described in Ref. 20.

Unfortunately such a calculation is rather difficult, and because the van der Waals energy is hardly affected by orthogonalization, our program handling nonorthogonal orbitals was never developed past a pilot stage. As the main limitation is that it can handle at most eight nonorthogonal, nondoubly occupied orbitals simultaneously, we were forced to divide up the calculations into smaller pieces.

From the perturbation results given in Tables I and II it is clear that in the long range a VB calculation, involving all structures that give an R^{-7} dependence,

TABLE III. Decomposition of the *VB* dipole moments for the linear geometry.[a] All dipole moments are in 10^{-5} a.u.[b]

R [bohr]	Exchange	H_2-overlap induction	He-induction[c]	(2, 0) disp	(1, 1) disp	Rest	$\langle\mu_{VB}\rangle$
4.0	1768.48	2870.56	1020.39(834.33)	384.21	−25.05	−349.99	5623.60
5.2	249.07	377.87	300.81(282.87)	51.92	−5.35	−63.93	910.39
5.6	121.96	184.18	214.89(208.97)	11.14	−3.39	−29.59	499.19
6.0	57.73	87.97	159.07(157.76)	−5.32	−2.07	−12.81	284.57
7.0	7.57	12.57	83.93(84.34)	−7.69	−0.71	−1.24	94.43
8.0	0.78	1.53	49.02(49.17)	−3.33	−0.26	−0.10	47.64
10.0	0.00	0.02	20.00(20.00)	−0.57	−0.05	0.00	19.40

[a]The decomposition is performed according to the definitions (i)–(iv) given in the text.
[b]Positive direction of the dipole moment corresponds with negatively charged H_2 and positively charged He.
[c]In parentheses the multipole expansion results are given, calculated as a sum of the R^{-4}, R^{-6}, and R^{-8} terms.

can be split. In the linear case, for instance, we see that a calculation based on the ground state and structures of $(z;\sigma_g)$ and $(z;\sigma_u)$ symmetry gives one term of the (1, 1) dispersion dipole on H_2 and one term of the (2, 0) dipole on He (and the He induction, of course). Another calculation, based on $(z;\sigma_g)$ and $(xz;\pi_{x,u})$ structures, gives a different term of the (2, 0) dipole on He and no contribution to the (1, 1) dipole. As far as perturbation theory holds, such terms are strictly additive.

Earlier[16] it was noted in energy calculations that a similar additivity also holds for shorter distances. Several tests on the dipole moment of this complex at $R = 5.2$ and 8.0 bohr have shown that here too the additivity predicted by long range theory holds excellently, even though at 5.2 bohr exchange and penetration are far from negligible. This makes it possible to partition the orbital set into subsets of different local symmetry and to divide the complete VB calculation into smaller ones based on choices out of these subsets guided by Tables I and II.

However, a complication arises here from the fact that the Tables I and II are derived under the assumption of orthogonal states and hence orthogonal orbitals. So, additivity holds only strictly in that case; or, in other words, the orbitals figuring in the resolvents of Tables I and II must be interpreted as orthogonalized orbitals. The orthogonalized orbitals can of course be expanded in terms of the original orbitals. Substituting these expansions into the resolvents, it follows that coupling matrix elements occur that are zero in the long range. The strength of these coupling matrix elements is determined by the intermolecular overlap of the orbitals involved, which is negligibly small in most cases. Such mixing does not occur for orbitals of different global symmetry ($C_{\infty v}$ and C_{2v} for the linear and the perpendicular case, respectively) which have zero overlap, and the corresponding parts of the resolvent are still additive.

The latter property was used when making a first partitioning of the VB calculation with the nonorthogonal orbitals. In the linear case we have included the dispersion structures of (σ, σ) type and those of (π, π) type in two separate VB calculations; in the perpendicular case we had to make a further splitting of the VB calculation. The number of orbitals in each VB calculation was restricted by inspecting the weight of the structures in the VB wavefunction of Geurts *et al.*[15] in which these orbitals occur. Moreover, we have performed numerous tests to check that no important overlap contributions were neglected and that additivity holds between the separate VB calculations.

IV. RESULTS AND DISCUSSION

In Tables III and IV the different contributions to the dipole moment are given for the linear and the perpendicular case, respectively. Note that the (1, 1) contribution is absent for the T shaped complex. Because this contribution is only 10% of the (2, 0) dipole for the linear geometry, a number in accordance with the findings of Byers Brown and Whisnant,[10,11] and because the (2, 0) dispersion itself is already very small, we decided that it was not worth the effort to calculate this small effect in the perpendicular case as well.

As will be shown in a second paper, the region responsible for the collision induced absorption in He–H_2 stretches from 4.5–8.0 bohr. We see that the two short range effects, exchange and H_2 overlap-induction, are dominant there, although the dipole moment in He induced by the permanent moments on H_2 is also sizable. This latter term has a strikingly good R^{-4} dependence down to $R = 5.2$ bohr. As far as the absence of higher multipole terms (R^{-6}, R^{-8}, etc.) is concerned, this can be understood since the hexadecapole and higher permanent moments of H_2 are relatively small.[21] What is surprising, however, is the absence of short range effects, while short range forces become nonnegligible at around 7.0 bohr, which can also be seen from the fact that the dispersion terms fail to have an R^{-7} dependence for distances shorter than 7.0 bohr. The (2, 0) dispersion even changes sign in that region.

Regarding a comparison with the results of Poll and Hunt[14] obtained from an interpretation of the experimental spectrum, we note that one can write:

$$\mu_{\parallel} \simeq A_{01} - \sqrt{2}A_{21} + \sqrt{3}A_{23},$$

$$\mu_{\perp} \simeq A_{01} + \tfrac{1}{2}\sqrt{2}A_{21} - \tfrac{1}{2}\sqrt{3}A_{23}.$$

TABLE IV. Decomposition of the VB dipole moments for the perpendicular geometry. All dipole moments are in 10^{-5} a.u. (see captions Table III).

R [bohr]	Exchange	H_2–overlap induction	He-induction	(2, 0) disp	Rest	$\langle \mu_{VB} \rangle$
4.0	1136.97	1412.02	−219.35(−364.63)	52.36	−132.96	2249.04
5.2	172.37	176.57	−116.23(−130.61)	−26.89	−22.57	183.25
5.6	84.21	85.67	−91.98(−97.55)	−23.87	−11.24	42.79
6.0	39.24	40.70	−72.58(−74.30)	−18.36	−5.34	−16.34
7.0	4.74	5.64	−40.65(−40.37)	−7.46	−0.93	−38.66
8.0	0.43	0.65	−23.89(−23.77)	−2.84	−0.23	−25.88
10.0	0.00	0.00	−9.80(−9.79)	−0.54	0.01	−10.33

Here the A values are the ones defined by Poll and Hunt in their parametrization of the dipole moment of an atom–diatom system; $\mu_{\parallel}$ stands for the dipole moment of the linear complex and $\mu_{\perp}$ for the dipole moment of the T shaped complex. Clearly, for the isotropic part A_{01} of the dipole moment one has

$$A_{01} \simeq \tfrac{1}{3}(\mu_{\parallel} + 2\mu_{\perp}) .$$

Since A_{01} has a short range component, as well as a long range component due to dispersion, the following parametrized form for A_{01} is physically reasonable:

$$A_{01} = C \exp[-R/\rho] + DR^{-7} .$$

The dispersion part is obtained by fitting $\frac{1}{3}(\mu_{\parallel} + 2\mu_{\perp})$ at large distances (7–10 bohr) to the form DR^{-7}, which goes quite well. The short range contribution is obtained by fitting the same expression at short distances (4.0–5.6 bohr) after the dispersion part is subtracted. We then find a good exponential behavior. In this manner the following values are resulting: $C = 38.8$ a.u., $\rho = 0.58$ bohr, $D = -61.8$ a.u. (The exchange dipole alone yields $\rho = 0.61$ bohr). The value of ρ is in reasonable agreement with the value $\rho = 0.624$ bohr quoted by Poll and Hunt[14]; more detailed fits including variations in the rotational and vibrational coordinates of H_2 are presented in a forthcoming paper.

The parameter A_{23} is mainly due to induction. From the formula derived in the appendix we get:

$$A_{23} = \sqrt{3}\, \alpha_0^{\mathrm{He}} \langle Q_2^{\mathrm{H_2}} \rangle R^{-4} .$$

As we have seen earlier, one gets essentially the same result for the He induction dipole whether we apply this formula or fit the VB He induction results at large distances, both methods give $A_{23} = 1.14/R^4$. Using the accurately computed values of Refs. 22 and 23 for α_0^{He} and $\langle Q_2^{\mathrm{H_2}} \rangle$, respectively, one gets $A_{23} = 1.16/R^4$.

Comparing the different contributions to the collision induced dipole, as given in Tables III and IV, one finds as the most important conclusion of this paper that a very good description of the collision induced dipole moment is obtained by including exchange, H_2-overlap induction and, as the only long range effect, the quadrupole induction dipole on the He atom. The two different short range effects have practically the same, exponential, distance dependence.

When looking at heavier rare gas systems one must keep in mind that the polarizability of the He atom is extraordinarily small. Therefore, one can expect for heavier rare gases the long range effects to be more important, but also the exchange and penetration to start at larger distances. In any case, it is clear from our results that the effects of short range forces on the collision induced spectra cannot be neglected.

ACKNOWLEDGMENT

We express our thanks to Professor J. D. Poll for suggesting this problem and for valuable discussions.

APPENDIX

In this appendix the matrix element $\langle 00 | \mu^{(1,0)} | 00 \rangle$ is expressed in a series in $1/R$. No assumption is made regarding the symmetries of the subsystems, the only condition is that they are neutral. Specializing the resulting expression to an atom-diatom system it becomes the well-known classical formula describing an isotropic polarizable charge in the field of permanent multipoles.

We will follow Fano and Racah's notation[24] in writing a Clebsch–Gordan series as an irreducible tensorial product, denoted by square brackets. The spherical harmonics $C_{lm}(\hat{r})$ used below have the phase of Condon and Shortley and are normalized to $4\pi/(2l+1)$.

We evaluate

$$\langle 00 | \mu^{(1,0)} | 00 \rangle = \langle 00 | (\mu^{\mathrm{A}} + \mu^{\mathrm{B}}) R_0 V + V R_0 (\mu^{\mathrm{A}} + \mu^{\mathrm{B}}) | 00 \rangle .$$

First the term $\langle 00 | \mu^{\mathrm{B}} R_0 V | 00 \rangle$ is considered, the other terms follow then by analogy. Because the monomer B is neutral, we may measure μ^{B} from any origin; we choose the center of mass of B.

Expanding R_0, and inserting the multipole expansion for V[17] we get:

$$\langle 00 | \mu_\nu^{\mathrm{B}} R_0 V | 00 \rangle = \sum_{l_a, l_b = 0}^{\infty} (-1)^{l_a} \binom{2L}{2l_a}^{1/2} \times (2L+1)^{1/2} R^{-L-1} {\sum_b}' \Delta E_{ob}^{-1} [\langle 0 | \mu^{\mathrm{B}} | b \rangle \times [\mathbf{C}_L(\hat{R}) \times [\langle 0 | \mathbf{Q}_{l_a}^{\mathrm{A}} | 0 \rangle \times \langle b | \mathbf{Q}_{l_b}^{\mathrm{B}} | 0 \rangle]^{(L)}]^{(0)}]_\nu^{(1)} . \tag{1}$$

Here: μ_ν^{B} is the νth spherical component of μ^{B},

$L = l_a + l_b$,

$\mathbf{R} = (R, \hat{R})$ is the vector pointing from the center of mass of A to the center of mass of B,

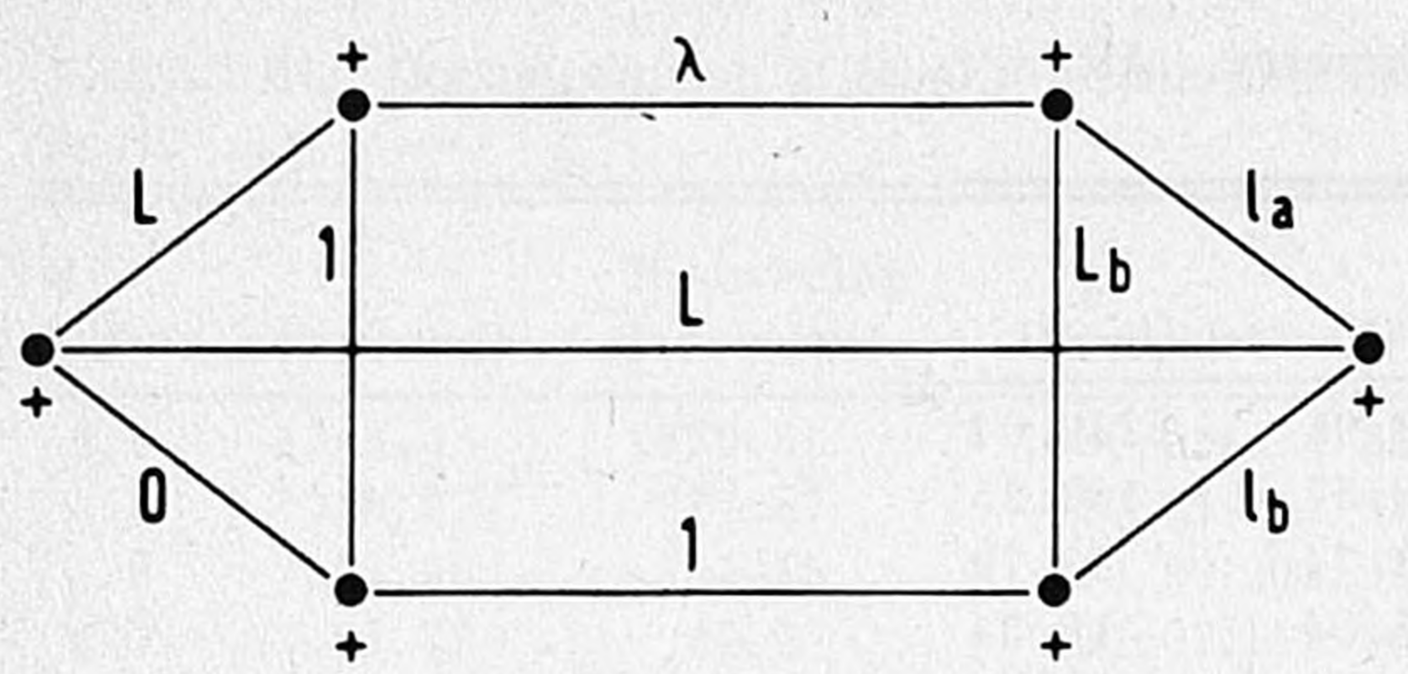

FIG. 1. Graph G representing the recoupling coefficient referred to in the appendix.

$$Q^{A}_{l_a m_a} = \sum_{\alpha \in A} q_\alpha r_\alpha^{l_a} C_{l_a, m_a}(\hat{r}_\alpha)$$ (a summation over the charges q_α belonging to molecule A and having position vectors $\mathbf{r}_\alpha = (r_\alpha, \hat{r}_\alpha)$),

$Q^{B}_{l_b m_b}$ as for A.

Instead of the irreducible product arising in this expression we would rather have the following one:

$$[[\langle 0 | \mu^B | b\rangle \times \langle b | \mathbf{Q}^B_{l_b} | 0\rangle]^{L_b} \times \langle 0 | \mathbf{Q}^A_{l_a} | 0\rangle]^{(\lambda)} \times \mathbf{C}_L(\hat{R})]^{(1)}_\nu \quad (2)$$

because here the irreducible tensors on B are coupled first, and hence we may be able to substitute the dipole/l_b-pole polarizability of B. Furthermore, this irreducible product gives the simplest possible behavior under rotation of the monomers.

One readily derives that the required recoupling coefficient is $[(2\lambda+1)(2L_b+1)(2L+1)]^{1/2} \times G$, where G is the graph given in Fig. 1. This graph breaks on three lines,[25] and so we get for the recoupling coefficient:

$$[(2\lambda+1)(2L_b+1)(2L+1)]^{1/2}(-1)^{\lambda+1+L} \begin{Bmatrix} \lambda & L & 1 \\ 0 & 1 & L \end{Bmatrix} \begin{Bmatrix} l_a & \lambda & L_b \\ 1 & l_b & L \end{Bmatrix}$$

$$= \left[\frac{(2\lambda+1)(2L_b+1)}{3}\right]^{1/2} \begin{Bmatrix} l_a & \lambda & L_b \\ 1 & l_b & L \end{Bmatrix}, \quad (3)$$

where the expressions between curly brackets are the usual Wigner $6j$ symbols.

Define the irreducible l_b-pole/l_b'-pole polarizability of B by:

$$\alpha^B_{(l_b, l_b')L_b} = \sum_b{}' \frac{[\langle 0 | \mathbf{Q}^B_{l_b} | b\rangle \times \langle b | \mathbf{Q}^B_{l_b'} | 0\rangle]^{(L_b)}}{E^B_0 - E^B_b} . \quad (4)$$

Then:

$$\langle 00 | \mu^B_\nu R_0 V + V R_0 \mu^B_\nu | 00\rangle = \frac{1}{\sqrt{3}} \sum_{l_a, l_b = 0}^{\infty} (-1)^{l_a} \binom{2L}{2l_a}^{1/2} R^{-L-1}$$

$$\times \sum_{\lambda, L_b} [(2\lambda+1)(2L_b+1)(2L+1)]^{1/2}$$

$$\times \begin{Bmatrix} l_a & \lambda & L_b \\ 1 & l_b & L \end{Bmatrix} (T_\nu + (-1)^\nu T^*_{-\nu}), \quad (5)$$

where:

$$T_\nu \equiv [[\alpha^B_{(1, l_b)L_b} \times \langle 0 | \mathbf{Q}^A_{l_a} | 0\rangle]^{(\lambda)} \times \mathbf{C}_L(\hat{R})]^{(1)}_\nu$$

and further one easily shows:

$$(-1)^\nu T^*_{-\nu} = (-1)^{-L_b + l_b + 1} [[\alpha^B_{(l_b, 1)L_b} \times \langle 0 | \mathbf{Q}^A_{l_a} | 0\rangle]^{(\lambda)} \times C_L(\hat{R})]^{(1)}_\nu .$$

To our knowledge this formula for the dipole moment induced on a molecule of arbitrary symmetry by another molecule, also of arbitrary symmetry, has not been given before. The vector T_ν has the following physical interpretation: a permanent moment $\langle 0 | \mathbf{Q}^A_{l_a} | 0\rangle$ on A induces an irreducible tensor of order L_b on B via the dipole/l_b-pole polarizability of B. These two monomer tensors couple to give a dimer tensor of order λ, which in turn couples with the geometrical tensor $\mathbf{C}_L(\hat{R})$ to the ν component of the vector $\mathbf{T}$.

If B is an atom (in a state $|\gamma_0 L_0 M_0\rangle$) the polarizability tensor (4) is a scalar:

$$\alpha^B_{(l_b, l_b')L_b} = \delta_{l_b l_b'} \delta_{L_b, 0} (2l_b+1)^{-1/2}$$

$$\times \sum_{\gamma_1 L_1} (-1)^{L_0 + L_1 - l_b} \{L_0, L_1, l_b\}$$

$$\times \frac{\langle \gamma_0 L_0 || Q_{l_b} || \gamma_1 L_1\rangle \langle \gamma_1 L_1 || Q_{l_b} || \gamma_0 L_0\rangle}{E_{\gamma_0 L_0} - E_{\gamma_1 L_1}}, \quad (6)$$

where $\{L_0, L_1, l_b\}$ is the triangular delta, and the double barred matrix elements are the usual reduced matrix elements introduced by applying the Wigner–Eckart theorem.

In the case of $l_b = 1$ the above definition for the dipole/dipole polarizability of an atom differs by a factor $\frac{1}{2}\sqrt{3}$ from the more usual definition:

$$\alpha^B_{(1,1)0} = \tfrac{1}{2}\sqrt{3}\, \alpha^B_0, \text{ where } \alpha^B_0 \equiv \frac{2}{3} \sum_b{}' \sum_i \frac{\langle 0 | r_i | b\rangle \langle b | r_i | 0\rangle}{E^B_b - E^B_0},$$

$$r_i = x, y, z .$$

If A is a linear molecule in a Σ state, one easily proves:

$$\langle 0 | Q^A_{l_a m_a} | 0\rangle = C_{l_a m_a}(\hat{R}_A) \langle Q^A_{l_a}\rangle ,$$

where $\hat{R}_A$ is the unit vector that specifies the orientation of A, and $\langle Q^A_{l_a}\rangle$ is the component of the l_a pole along the molecular axis. If A is a homonuclear diatomic, only even l_a values occur. One finally arrives at:

$$\langle 00 | \mu^{He}_\nu R_0 V + V R_0 \mu^{He}_\nu | 00\rangle$$

$$= \frac{1}{\sqrt{3}} \sum_{l_a} [(l_a+1)(2l_a+1)(2l_a+3)]^{1/2}$$

$$\times R^{-l_a-2} \alpha^{He}_0 \langle Q^{H_2}_{l_a}\rangle [\mathbf{C}_{l_a}(\hat{R}_{H_2}) \times \mathbf{C}_{l_a+1}(\hat{R})]^{(1)}_\nu . \quad (7)$$

Note that this formula has been derived without using the gradient formula, as is usually done.[8,9]

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